

Study of Phase Transitions in the Ferroelectric Material $\text{Na}_3\text{MoO}_3\text{F}_3$ by *in situ* X-Ray Powder Diffraction Techniques and ^{19}F and ^{23}Na MAS NMR

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Beamline(s): X7B

Introduction: $\text{Na}_3\text{MoO}_3\text{F}_3$ belongs to the cryolite oxyfluoride family of compounds. The current work is a part of an ongoing study of the cryolite oxyfluoride family of perovskites such as $\text{Na}_3\text{MoO}_3\text{F}_3$. They are ferroelectric and ferroelastic materials with structural similarities to the double perovskite Cryolite (Na_3AlF_6), with A and B sites alternatively occupied by Na and Mo or W (**Figure 1**). $\text{Na}_3\text{MoO}_3\text{F}_3$ undergoes two-phase transitions: one from a monoclinic α -phase to another monoclinic phase, the β -phase, (at 130°C) and to a paraelectric cubic phase (γ -phase) at higher temperature (at 530°C) [1]. Variable temperature MAS NMR results suggest that the first phase transition starts at around 130°C and that the mixed phases co-exist up to 260°C [2]. The actual nature of the phase transition and the role played by the motion of the $\text{MoO}_3\text{F}_3^{3-}$ octahedra are some of the important aspects of this current work. There is also a lack of structural data on this compound.

Methods and Materials: $\text{Na}_3\text{MoO}_3\text{F}_3$ has been prepared using standard solid-state reactions of a stoichiometric mixture of NaF and MoO_3 . An *in situ* variable temperature X-ray diffraction pattern was collected using the X7B synchrotron beamline.

Results: The variable temperature X-ray diffraction pattern acquired at the NSLS shows (**Figure 2**) a gradual phase change from a monoclinic α -phase to the β -phase with a change in the unit cell parameters. The space group remains the same ($P2_1$). The figure shows the co-existence of the both phases, which leads to a thermal hysteresis in the phase transition, as suggested by the solid-state NMR results [2].

Conclusions: This work has led to a more accurate determination of the phase transition temperature. Careful analysis of the data should also reveal the temperature dependent changes of the unit cell parameters and atomic positions. Future work on these series of oxyfluorides should also help to clarify the role of different driving forces behind the phase transitions, which ultimately leads to the loss of ferroelectric properties at 530°C .

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References: [1] J. P. Chaminade, M. C. Marzal, J. Ravez, P. Hagenmuller "Ferroelastic and Ferroelectric behavior of the oxyfluoride $\text{Na}_3\text{MoO}_3\text{F}_3$ " Mat. Res. Bull. **21**, 1209, 1986; [2] L. S. Du "Application and Theoretical Study of Solid-state NMR to Inorganic Fluorides and Oxyfluorides" Ph.D. Thesis, SUNY Stony Brook, Department of Chemistry, 2000.

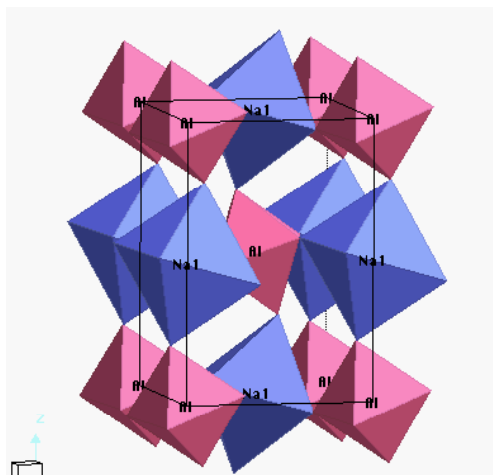


Figure 1. Na_3AlF_6 or cryolite has both cubic and octahedral coordination environments for sodium. The oxyfluorides have a similar cation environment with $\text{MoO}_3\text{F}_3^{3-}$ octahedra in place of the AlF_6^{3-} octahedra.

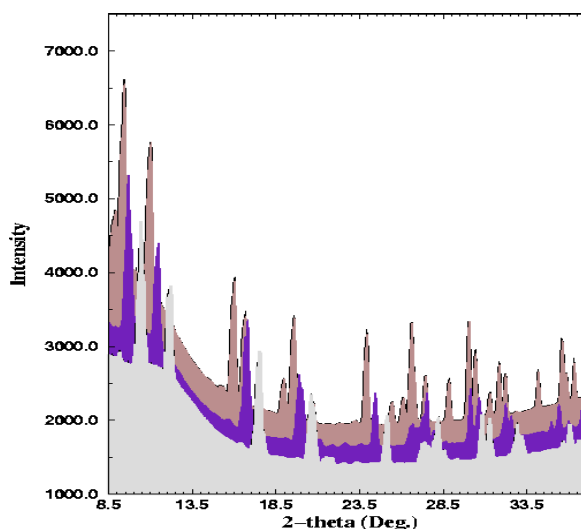


Figure 2. The Synchrotron *in situ* powder diffraction pattern at room temperature, 130°C and 170°C from back to front.